Non-linear response of single-molecule magnets: field-tuned quantum-to-classical crossovers

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Quantum nanomagnets can show a field dependence of the relaxation time very different from their classical counterparts, due to resonant tunneling via excited states (near the anisotropy barrier top). The relaxation time then shows minima at the resonant fields $H_n \propto nD$ at which the levels at both sides of the barrier become degenerate (D is the anisotropy constant). We showed that in Mn_{12}, near zero field, this yields a contribution to the *nonlinear* susceptibility that makes it qualitatively different from the classical curves [Phys. Rev. B **72**, 224433 (2005)]. Here we extend the experimental study to finite dc fields showing how the bias can trigger the system to display those quantum nonlinear responses, near the resonant fields, while recovering an classical-like behaviour for fields between them. The analysis of the experiments is done with heuristic expressions derived from simple balance equations and calculations with a Pauli-type quantum master equation.

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I. INTRODUCTION

Single-molecule magnets are metal-organic clusters containing a magnetic core surrounded by a shell of organic ligands which isolates the clusters from one another (see, e.g., Refs. [1]). The most studied is Mn_{12}, whose core contains eight Mn^{3+} and four Mn^{4+} ions strongly coupled via super-exchange interactions. This gives a ground state spin $S = 10$, while the large Jahn-Teller distortion on the Mn^{3+} sites leads to a strong uniaxial anisotropy. The energy levels have a bistable structure $\varepsilon_m \sim -D\,m^2$ (at zero field) with an energy barrier $U = \varepsilon_0 - \varepsilon_S \simeq 70\,\mathrm{K}$ to be overcome for the spin reversal. At low temperatures, these systems show the typical behaviors of superparamagnets, such as blocking or hysteresis, yet at a much smaller scale of size. In addition, they form molecular crystals in which all molecules are nearly identical and, in the case of Mn_{12} acetate, have their anisotropy axes $\boldsymbol{z}$ parallel to the crystallographic $\boldsymbol{c}$ axis.

These properties make molecular magnets model systems to investigate whether quantum phenomena, like tunneling, survive in mesoscopic systems [2]. As is well-known, tunneling probabilities decrease exponentially with the height of the barrier to be tunneled through (height that grows with the system size) [3]. At the same time, external perturbations can induce decoherence that degrades the quantum behavior [4, 5]. Furthermore, an external magnetic field H_z detunes energetically the initial and final states for tunneling (i.e., those having $+m$ and $-(m+n)$ spin projections along $\boldsymbol{z}$). Actually, many experiments have shown that tunneling takes place at those fields where states of opposite orientation are degenerate, $H_n \simeq n\,H_1$ ($n = 0, 1, 2, \ldots$ with $H_1 = 2g\mu_{\mathrm{B}}D \simeq 4200\,\mathrm{Oe}$ in Mn_{12}), whereas it is suppressed for intermediate fields [6, 7, 8].

Such a *resonant* tunneling enables the spins to approach faster their equilibrium state, giving rise to steps in the hysteresis loops around $H_z = H_n$ [9] and to maxima in the linear dynamical susceptibility χ_1. In our previous work [10, 11], we found that resonant tunneling at $H_z = 0$ induces an extra contribution to the nonlinear response χ_3, making it larger (in magnitude) than the equilibrium one and having peaks reversed with respect to the classical predictions [12, 13]. In Refs. [10, 11] the dependence of the response on temperature, frequency, and orientation at zero field was studied. In this article we show how the tunneling contribution to the nonlinear response can be switched on and off by varying an external field, tuning and breaking successively the resonances.

II. EXPERIMENTAL DETAILS

Single crystals of Mn_{12} acetate were grown following the same procedure described in [11]. In order to increase the signal, the magnetic measurements were done on a collection of oriented and glued crystals. In our previous experiments [10, 11] we extracted the zero-field $\chi_3(\omega)$ by fitting the dc field dependent $\chi(\omega)$ to a parabola. Clearly, this method is not applicable to study how χ_3 depends on the external magnetic field itself. For this reason, in the present experiments we resorted to the more traditional method of measuring non-linear susceptibilities by detecting the different harmonics $\chi_2(2\omega)$ and $\chi_3(3\omega)$ of the response. In the absence of bias field one had $\chi_2 \equiv 0$ (see below). A nonzero H_z, however, makes χ_2 the leading nonlinear term, and we will mainly focus on it.

The fields, both dc and ac, were applied *parallel* to the common anisotropy direction $\boldsymbol{z}$ of the clusters. We employed the susceptibility option of a commercial multipurpose measuring platform (PPMS) which uses a conventional inductive method. It enables applying ac fields of amplitude $h_0 \leq 17\,\mathrm{Oe}$, and to selectively detect several harmonics of the exciting frequency $\omega/2\pi < 10\,\mathrm{kHz}$. To

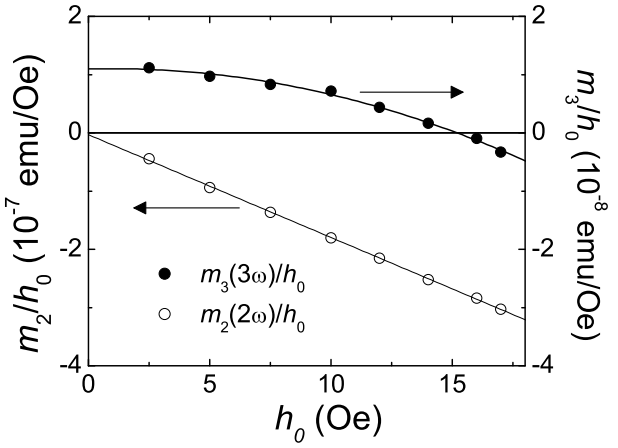

FIG. 1: Illustration of the method employed for measuring the nonlinear susceptibilities (here $T = 8\,\mathrm{K}$, $H_z = 100\,\mathrm{Oe}$, and $\omega/2\pi = 2\,\mathrm{kHz}$). $\chi_2(2\omega)$ and $\chi_3(3\omega)$ are obtained, respectively, from the slope and the quadratic coefficient of the second $m_2(2\omega)/h_0$ and third $m_3(3\omega)/h_0$ harmonics of the output signal, measured as a function of the ac field amplitude h_0.

separate the intrinsic nonlinear response of the sample from the possible contamination due to non-perfect harmonicity of the exciting ac coil, we measured the output signals $m_2(2\omega)/h_0$ and $m_3(3\omega)/h_0$ at several h_0. This gives the sought-for intrinsic contributions χ_2 and χ_3 as the terms proportional to h_0 and h_0^2 respectively. An example of this procedure is shown in Fig. 1.

III. RESULTS AND MODELIZATION

The so-measured linear and nonlinear susceptibilities of Mn_{12} at $T = 8\,\mathrm{K}$ are shown in Fig. 2. The frequency-dependent χ_1 shows maxima near the resonant fields, where it approaches the equilibrium χ_1^{eq}. We also display (panel b) the second and third harmonic components measured at $\omega/2\pi = 2\,\mathrm{kHz}$. (The high noise-to-signal ratio prevented from obtaining reliable χ_3 data for $H_z > 1\,\mathrm{kOe}$.) The *equilibrium* nonlinear susceptibilities, also shown, were obtained differentiating χ_1^{eq}, measured at the lowest frequency $\omega/2\pi = 1\,\mathrm{Hz}$.

We clearly see that the magnitudes of the harmonics increase in the neighborhood of the resonant fields $H_0 = 0$, H_1 and H_2, where states of opposite S_z are degenerate and the tunnel channels open. Besides, in contrast with the behavior of χ_1, both χ_2 and χ_3 become, near H_0, larger than χ_2^{eq} and χ_3^{eq}. Thus, when resonant tunnel sets on, the multi-harmonic response of these molecular clusters is enhanced.

In order to understand these results we have derived simple expressions for the susceptibilities. This was done by solving, as in Ref. [13], a system of balance equations for the net population of the two anisotropy potential wells:

$$\chi_1(\omega) = \chi_1^{\mathrm{eq}}\frac{1}{1+\mathrm{i}\,\omega\tau}\,, \qquad \chi_2(2\omega) = \chi_2^{\mathrm{eq}}\frac{1}{1+2\mathrm{i}\,\omega\tau} - \chi_1^{\mathrm{eq}}\frac{\mathrm{i}\,\omega\tau'}{(1+\mathrm{i}\,\omega\tau)(1+2\mathrm{i}\,\omega\tau)} \tag{1}$$

$$\chi_3(3\omega) = \chi_3^{\mathrm{eq}}\frac{1}{1+3\mathrm{i}\,\omega\tau} - \chi_1^{\mathrm{eq}}\frac{\frac{1}{2}\mathrm{i}\,\omega\tau''}{(1+\mathrm{i}\,\omega\tau)(1+3\mathrm{i}\,\omega\tau)} - \chi_2^{\mathrm{eq}}\frac{2\mathrm{i}\,\omega\tau'}{(1+2\mathrm{i}\,\omega\tau)(1+3\mathrm{i}\,\omega\tau)} - \chi_1^{\mathrm{eq}}\frac{2\mathrm{i}(\omega\tau')^2}{(1+\mathrm{i}\,\omega\tau)(1+2\mathrm{i}\,\omega\tau)(1+3\mathrm{i}\,\omega\tau)}\,. \tag{2}$$

The equilibrium $\chi_k^{\mathrm{eq}} = (\mathrm{d}^k M_z/\mathrm{d}H_z^k)/k!$ are the derivatives of the magnetization curve, while τ, τ', and τ'' are the relaxation time and its corresponding field-derivatives (all evaluated at the working field H_z). At $H_z = 0$ we have $\chi_2^{\mathrm{eq}} \equiv 0$ [since $M_z(H_z) = -M_z(-H_z)$] as well as $\tau' \equiv 0$ [from $\tau(H_z) = \tau(-H_z)$]. Then $\chi_2(2\omega) \to 0$ as $H_z \to 0$, while in χ_3 the last two terms vanish. Therefore these equations extend the expressions of Ref. [13] to nonzero bias fields.

The first Eq. (1) gives the ratio $\chi_1/\chi_1^{\mathrm{eq}} < 1$. Besides χ_1 depends, via the product $\omega\tau$, on how far the spins are from thermal equilibrium. By contrast, the nonlinear susceptibilities χ_2 and χ_3 include also terms depending on τ' and τ'', i.e., on how sensitive τ is to changes of H_z. As a result, the relaxation time does not simply "renormalize frequency", as occurs with χ_1, but it modifies the magnitudes of the nonlinear responses. This effect is missed in modelizations of the nonlinear susceptibility that fail to include the field derivatives of τ [15]. As we discuss next, extending our arguments at $H_z = 0$ of [10, 11], it is this property that makes the quantum χ_2 and χ_3 qualitatively different from the classical ones.

According to Eq. (1), the relaxation time of the magnetic clusters can be estimated from χ_1 as $\chi_1''/\omega\chi_1'$ where χ_1' and χ_1'' are the real and imaginary components of the first harmonic. This τ is shown in the inset of Fig. 2. The data show minima at the resonant fields, in contrast with the monotonous behaviour of τ in classical spins. At zero field and finite temperatures, Mn_{12} spins are able to tunnel between those excited magnetic states ($m \sim 2$–4) for which such process is not blocked by the internal bias caused by dipolar and hyperfine interactions [16]. This results in a effective barrier reduced by a few magnetic

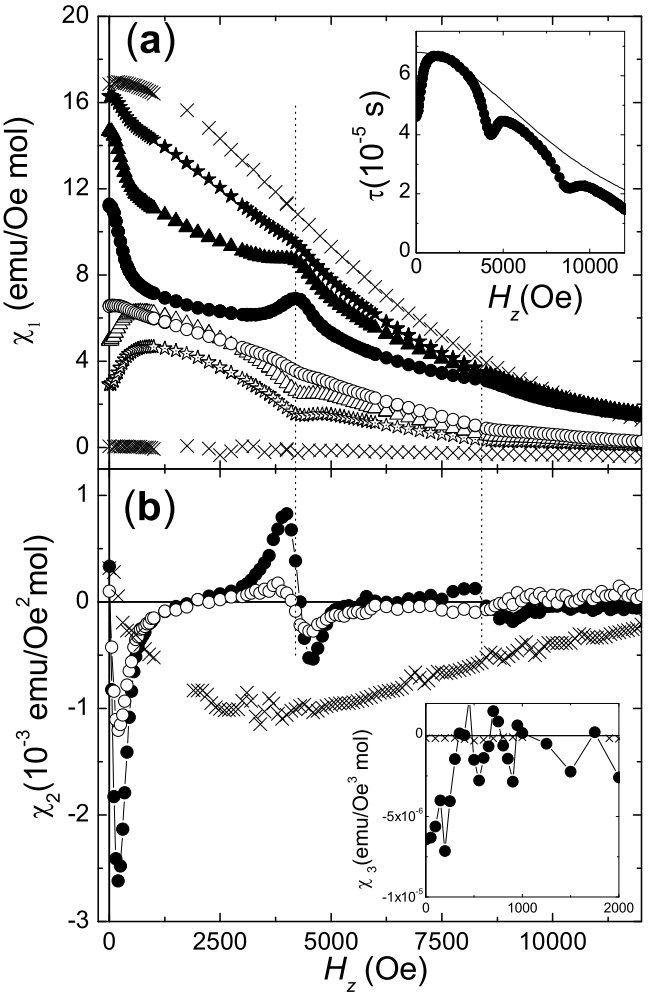

FIG. 2: Upper panel: linear susceptibility of Mn_{12} measured at $T = 8\,\mathrm{K}$ versus a magnetic field applied parallel to the anisotropy axis. ×, $\omega/2\pi = 1\,\mathrm{Hz}$ (∼equilibrium); ⋆, 500 Hz; △, 1 kHz; •, 2 kHz. Solid symbols, real parts; open symbols, imaginary parts. The inset shows the relaxation time τ, as obtained from $\chi_1''/\omega\chi_1'$ [see Eq. (1)] as well as calculated for classical spins (line) [14]. Lower panel, second harmonic susceptibility measured at the same temperature. • and ∘, $\chi_2'(2\omega)$ and $\chi_2''(2\omega)$ at 2 kHz; ×, equilibrium $\chi_2^{\mathrm{eq}} = (\mathrm{d}\chi_1^{\mathrm{eq}}/\mathrm{d}H_z)/2$. Inset: •, $\chi_3'(3\omega)$ at 2 kHz; ×, $\chi_3^{\mathrm{eq}} = (\mathrm{d}^2\chi_1^{\mathrm{eq}}/\mathrm{d}H_z^2)/6$. The dotted vertical lines mark the resonant fields $H_1 \simeq 4200\,\mathrm{Oe}$ and $H_2 = 2\,H_1$.

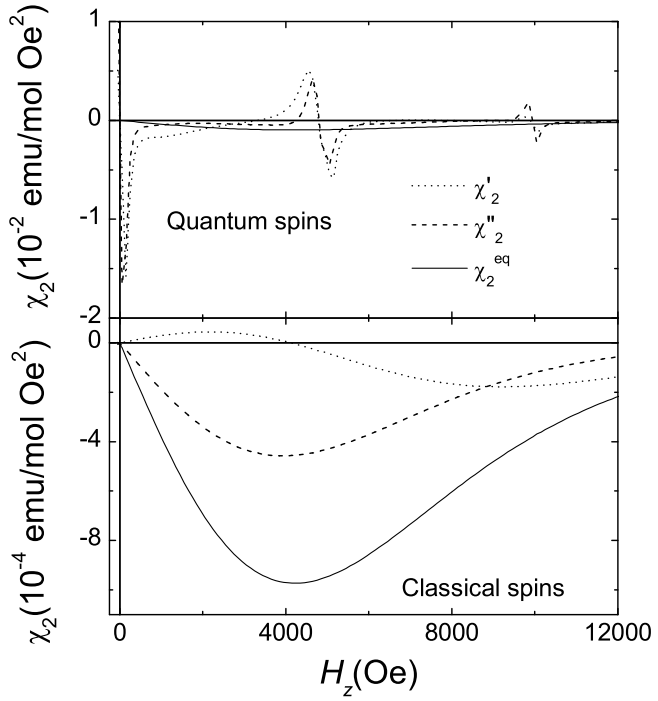

FIG. 3: Theoretical calculations of $\chi_2(2\omega)$ [Eq. (1)] for quantum and classical spins. In the latter case, we used Brown's classical formula for τ [14] and in the former τ was calculated by solving Pauli's quantum master equation, as described in [16]. Notice the difference in the χ_2 axis scale (the solid equilibrium curve is the same in both panels).

levels, say $U \sim \varepsilon_{\pm 3} - \varepsilon_{\pm S}$, so that the thermo-activated relaxation gets faster ($\delta U \sim 4\,\mathrm{K}$). Tunneling is however suppressed as soon as the external bias $\xi_m = 2g\mu_{\mathrm{B}} m H_z$ exceeds the tunnel splitting Δ_m, slowing down the relaxation (the full barrier has to be overcome). As a result, τ is minimum at zero field, whence $\tau'' > 0$, while τ' changes sign from < 0 to > 0.

The same features are repeated every time the field brings magnetic levels again into resonance $H_n = n \times (2g\mu_{\mathrm{B}})D$. Therefore, tunneling becomes, at any crossing field, an additional source of nonlinear response via τ' and τ''. Besides, accounting for the signs of the τ derivatives and Eqs. (1) and (2), one sees that the sign of the nonlinear susceptibilities can be reversed with respect to the classical ones. (In the classical model τ decreases monotonically with increasing field [14], inset of Fig. 2, giving $\tau'' < 0$ and $\tau' < 0$ for any H_z; the same occurs in a quantum thermoactivation model not including the possibility of tunneling [17, 18]).

It is interesting that both behaviors can be obtained in our case just varying the external field. For fields between resonances, tunneling becomes blocked for *all* states and the spins reverse by thermal activation over the total ("classical") energy barrier. But when a crossing field is approached, the strong nonlinearity of τ shows up with its characteristic contribution to the nonlinear susceptibilities via τ' and τ''.

To confirm this interpretation we have computed the nonlinear responses from Eqs. (1) and (2) but incorporating the relaxation time obtained by solving a Pauli quantum master equation (as in Ref. 16). The results (Fig. 3) show that the quantum contribution to $\chi_2(2\omega)$ is dominant near the resonances. This is due to the smallness of the tunnel splitting of the relevant states for our Mn_{12} sample: $\Delta_4 \sim 2 \times 10^{-2}\,\mathrm{K}$ and $\Delta_2 \sim 7 \times 10^{-1}\,\mathrm{K}$. This means that the fields required to block tunnel via these levels, albeit relatively small ($\sim 20\,\mathrm{Oe}$ and $1000\,\mathrm{Oe}$, respectively), give rise to relatively large changes in τ, and hence, large τ' and τ''. In the "classical" regime,

by contrast, the scale of change of τ is determined by the anisotropy field $H_{\rm a} \sim (2S-1)H_1$. As this is very large in Mn_{12} ($\simeq 95\,$kOe), one has a comparatively slow decrease of τ with H_z. This correspond to small values of the derivatives τ' and τ'' and in turn of the classical (non-tunnel) nonlinear susceptibilities.

It is also worth mentioning that the tunnel splittings, which determine the width of the τ vs H_z resonances, are further broadened by dipolar and hyperfine interactions [16]. In fact, the master-equation calculations tell us that tunneling via lower lying states would give rise to enormous spikes in χ_2 ($\Delta_{10} \sim 7\times10^{-10}\,$K for the ground state). However, these peaks are also very fragile, being easily suppressed by environmental bias fields and therefore not observed experimentally.

IV. SUMMARY AND CONCLUSIONS

We have studied experimentally the nonlinear susceptibilities of a Mn_{12} acetate molecular magnet in the presence of a longitudinal field H_z. The standard method of measuring the harmonics of the response to an oscillating field $h_0\cos(\omega t)$ has been employed. By using several amplitudes h_0 we managed to isolate the genuine nonlinear susceptibilities χ_2 and χ_3 (oscillating with $2\omega t$ and $3\omega t$). The low signal-to-noise ratio (in spite of gluing several single crystals) prevented from obtaining good χ_3 data; fortunately, we obtained nice curves for χ_2, which is the leading nonlinear term when a bias field is applied.

The analysis and interpretation of the susceptibility curves was done with help from expressions derived with a simple system of balance equations (for the potential well populations). At variance with previous formulae, the field derivatives of the magnetic relaxation time are captured by our expressions. This, together with the known strong effect on $\tau(H_z)$ of resonant tunneling near the barrier top, permitted to understand the experimental phenomenology. We also plugged in those equations the $\tau(H_z)$ obtained solving a Pauli quantum master equation for Mn_{12}, supporting this interpretation.

Near the resonant fields H_n (matching the levels at both wells) the χ_2 vs. H_z curves neatly amplify the resonant tunnel, as this entails large $\mathrm{d}\tau/\mathrm{d}H_z$. For fields in between the H_n's, tunnel is blocked and the response is governed by the thermo-activation over the total barrier, as in the classical case. This does not give such large τ', while its sign is reversed with respect to the tunnel contribution. Thus the sensitivity of χ_2 to the local features of the $\tau(H_z)$ curve provides an alternative method to asses if tunneling plays a role in the relaxation of a superparamagnet; and if so, in which field ranges it does take place.

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